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# review OF RECENT DEVELOPMENTS

## Corrosion and Compatibility

W. E. Berry • February 28, 1969



### CORROSION OF ALUMINUM ALLOYS

The development of inhibitive primer coatings for aluminum is discussed in a final report issued by IIT Research Institute.(1) Two effective organic inhibitors were developed: (1) alizarin, which forms a strongly bonded chelate with aluminum oxide, and (2) metallo-organic compounds containing chromium, zinc, arsenic, and antimony. The effect of the inhibitors was to prevent the underfilm spread of corrosion from a damaged area. Alizarin acted to stabilize the aluminum oxide layer by direct reaction, while the metallo-organics probably acted at cathodic areas to prevent hydrogen evolution. Alizarin also improved the adhesion of the primer to the aluminum.

The Australians have studied the effect of shot peening on the stress-corrosion cracking behavior of high-strength aluminum-alloy D.T.D. 5054 (intermediate in composition to American alloys 7075 and 7076).(2) The specimens were shot peened with 0.22-inch, rust-free chilled shot to an Almen Intensity of 0.008 (Almen gage No. 2). X-ray diffraction studies indicated a surface compressive layer to a depth of 6 mils, with the balancing tensile stresses distributed uniformly throughout the remainder of the cross section. Short transverse specimens were stressed in a single-cantilever beam-testing machine in a solution containing 0.5N NaCl and 0.005N $NaHCO_3$. The shot peening markedly improved the stress-corrosion cracking resistance of extruded, heat-treated, and cold-formed material.

### CORROSION OF IRON-BASE ALLOYS

#### Alloy Steels

The effect of high-velocity steam on tube bends in once-through steam generators was examined in a unit operated for 10 years by Babcock and Wilcox.(3) The steam generator was constructed of 3/4-in.-OD, 5/16-in.ID carbon molybdenum steel (SA209) tubing. Operating for approximately 8500 total hours, the pressure range was 500 to 6000 psi and the temperature range was 450 to 950 F. Based on the results of visual and low-power-magnification examination plus thickness measurements of tube samples, there was no evidence of internal erosion by the steam.

Fatigue-crack propagation tests on 9Ni-4Co-0.25C, 12Ni maraging, and 18Ni maraging steels in dry air and 3.5 percent NaCl solutions have been conducted by the Naval Research Laboratory.(4) Single-edge-notched specimens were cycled zero-to-tension in cantilever bending. Significant differences were observed in the fatigue-crack growth-rate characteristics of the three steels at the same yield-strength level (180 ksi). The fatigue-crack growth in all three steels was accelerated by the NaCl environment, but only to a limited extent. The greatest increase in crack-growth rate was less than one order of magnitude and occurred under low stress intensity ($\Delta K$ = 40 ksi/in.$^2$). The crack-growth rates were similar in air and NaCl at high stress intensity ($\Delta K$ = 100 ksi/in.$^2$). There was no correlation between the fatigue-crack growth behavior in NaCl and the stress-corrosion cracking parameter ($K_{Iscc}$) for these steels. This was attributed to the fact that cyclic loading at 5 cpm did not allow sufficient time for stress-corrosion cracking, which is time dependent, to cause any significant effect on the fatigue-crack growth in these steels.

The marine corrosion behavior of several high-strength steels has been studied by the International Nickel Company.(5) Corrosion rates obtained after 1 year's exposure are summarized as follows:

| Alloy | Corrosion Rate, mils/year: Atmospheric Exposure, 80 ft(a) | Atmospheric Exposure, 800 ft(a) | Seawater Exposure, 0.5 fps | Seawater Exposure, 2 fps | Seawater Exposure, 130 fps(b) |
|---|---|---|---|---|---|
| 18Ni maraging | 0.6 | 0.4 | 2.5 | 7 | 90 |
| 12-5-3 maraging | 0.4 | 0.3 | Pitted | Pitted | 42 |
| HY-80 | 1.4 | 1.0 | 3.7 | 12 | 57 |
| 4340 | 1.3 | 0.9 | 4.3 | -- | 140 |
| Mild steel | 5.1 | 1.2 | 4.0 | 9 | 180 |

(a) From ocean.
(b) 30-Day exposure.

Pits in the 12-5-3 maraging steel exposed to seawater ranged up to 35 mils in depth after 1 year's exposure. The application of cathodic protection eliminated the pitting. At high velocities of 130 fps, all steels exhibited high corrosion rates in seawater, but, as in the other environments, the high-strength steels were more corrosion resistant than mild steel. Stress-corrosion tests in a sea shore atmosphere (U-bends) produced cracking in the 18Ni maraging steel (250-ksi yield strength) and the 4340 steel (240-ksi yield strength) but not in the 12-5-3 maraging steel (205-ksi yield strength). U-bends of all three steels cracked in seawater. Cathodic protection improved the resistance to cracking when steel was used as the anode material, but caused hydrogen embrittlement when zinc anodes were used.

A new environmental cause of stress-corrosion cracking of mild and low-alloy steels has been described by the Japanese.(6) Transgranular cracking occurred in U-bend specimens within 1 week's

exposure to water at 104 F in an autoclave that was pressurized with 35-psi carbon dioxide and 178-psi carbon monoxide.

Stainless Steels

The hydrogen embrittlement of stainless steel has been studied by the Lawrence Radiation Laboratory.[7] Notched and unnotched tensile bars of Types 304L and 310 stainless steel were fractured in hydrogen or helium at 10 ksi and ambient temperature. The results indicated that hydrogen embrittlement occurs in an austenitic steel that is unstable with respect to the formation of strain-induced $\alpha$ (bcc) and $\epsilon$ (hcp) martensite when plastically strained in high-pressure hydrogen. A stable austenitic steel (Type 310) was not embrittled under these same test conditions.

The effect of explosive shocking on the corrosion and stress-corrosion cracking behavior of Types 304 and 310 stainless steel has been studied at Du Pont.[8] The pressures of explosive shocking ranged from 90 to 550 kb. The intergranular corrosion of the two steels in boiling nitric acid and ferric sulfate-sulfuric acid was only mildly affected by explosive shocking of solution-annealed or sensitized material. Stress-corrosion tests of up to 1100 hours in 42 percent boiling $MgCl_2$ on as-explosively-shocked pieces (no external applied stress) revealed that stress-corrosion cracking due to residual stresses occurred above 200 kb in Type 304 stainless steel and above 300 kb in Type 310 material.

The effect of surface preparation on the stress-corrosion cracking behavior of Type 310 stainless steel has been studied by The Ohio State University.[9] Wire specimens were vacuum annealed 2 hours at 1150 C (2100 F) and then were given various surface treatments. Stressed specimens then were exposed to boiling 42 percent $MgCl_2$. The times to failure followed a log-normal distribution. The mean times to failure (50 percent failed) as a function of surface preparations for specimens exposed at 90 percent of yield strength are summarized as follows:

| Surface Preparation | Mean Time to Failure, minutes |
|---|---|
| Vacuum annealed | 863 |
| Smooth mechanical polish | 708 |
| Electrochemical polish | 413 |
| Medium mechanical polish | 246 |
| Chemical polish | 226 |
| Rough mechanical polish | 202 |

The results were interpreted to mean that time to cracking was influenced by surface roughness, which affected the reduction reaction, i.e., reduction occurred less easily on smooth surfaces, thereby minimizing the anodic reactions associated with crack initiation and propagation.

## CORROSION OF MAGNESIUM ALLOYS

Research has been conducted at Redstone Arsenal on self-healing protective coatings for magnesium alloys.[10] The metal substrate used was AZ31B magnesium. Coatings were evaluated in 5 percent salt spray at 95 F. Gaseous diffusion, reactive solutions, and electrochemical methods were investigated. The first two methods were not successful. Success was achieved with an electrochemical method employing dc or ac to apply a coating from a bath containing 300 g/l ammonium bifluoride, 80 g/l ammonium metavanadate, and 20 to 100 g/l additives (8 different inorganic and organic compounds). These coatings survived 1 month's exposure in 5 percent salt spray, with no accelerated attack at scribe marks through the coating. The healing properties of the coating are attributed to the vanadium, but the mechanism of protection has not yet been established.

## CORROSION OF NICKEL-BASE ALLOYS

The effects of stress, thermal cycling, and isothermal exposure on the oxidation and mechanical properties of nickel-base alloys have been reported by Bendix.[11] Exposure times ranged up to 600 hours at temperatures of 1400, 1600, 1800, and 2000 F. TD-Nickel-Chromium (20Cr-2.5$ThO_2$) had superior no-load oxidation resistance, but was sensitive to stress and oxidized internally at temperatures above 1600 F. DH-242 (19Cr-1.2Cb + Ta) had good oxidation resistance and ductility retention, but was limited to small loads because of excessive elongation at temperatures greater than 1600 F. Hastelloy X (22Cr-18.5Fe-9Mo) had fair oxidation resistance and ductility retention despite a comparatively high spall rate. Cyclic oxidation was substantially more severe than steady-state isothermal oxidation for all materials studied.

The corrosion of nickel-base alloys in 1500 F combustion gases from high-sulfur diesel fuel has been studied at Westinghouse Research Laboratories.[12] Chromium was found to be the major contributor to oxidation resistance in this environment, and its effect was optimum at the 20 to 30 percent level. Of the commercial alloys studied, PDRL-163 and Unitemp 1753 were the most resistant while Alloy 713C, Udimet 700, and Inconel 700 were the least resistant. The additions of 0.1 to 0.3 percent lanthanum or yttrium to commercial alloys of the Udimet types effected a marked improvement in oxidation resistance

## CORROSION OF REFRACTORY MATERIALS

The corrosion of refractory materials in fluorine and HF at temperatures to 5200 F has been reported by IIT Research Institute.[13] The tests were conducted in argon-6.5 volume percent fluorine and argon-10 volume percent HF at velocities of 400 fps. The following materials were evaluated: tungsten, tantalum, rhenium, iridium, tungsten-iridium, tungsten-rhenium, rhenium-iridium, hafnium-tantalum, graphite, TaN, HfN, $HfB_2$, $ZrB_2$, $HfB_2$-SiC, $ZrB_2$-SiC-C, HfC-C eutectic, and TaC-C eutectic. Corrosion in fluorine was 2 to 10 times greater than in HF. Of the metals, iridium had the lowest corrosion rate in fluorine at temperatures greater than 3500 F (about 0.2 mil/min), while tantalum had the highest rate (about 3.5 mils/min). Of the nonmetallic materials, graphite and carbides had the lowest corrosion rates in fluorine at about 1.5 mils/min, while the HfN and TaN had the highest rates at about 3.5 mils/min.

The results of a program to develop oxidation-resistant hafnium alloys have been summarized in a final report by IIT Research Institute.[14] A number of quaternary and higher alloys based on the Hf-(20 to 30)Ta system met the goal of 100 hours' life in air at 2500 F. However, most of these alloys oxidized rapidly at 1600 F, presumably because of

the inability of the alloy to heal cracks in the oxide at low temperatures. Alloys in the Hf-Ta-Cr-B-Al system resisted oxidation at both 1600 and 2500 F, with the optimum composition being Hf-24.5Ta-0.66B-1.2Cr-0.12Al.

CORROSION OF SEVERAL ALLOY SYSTEMS

The mechanisms of sand and dust erosion in gas-turbine engines is being studied at Solar.[15] Candidate materials were impacted at equivalent energy levels by $Al_2O_3$ and Arizona road dust (principally $SiO_2$) of the same particle size (about 50 μ). Maximum erosion occurred at impingement angles of 30 to 37.5 degrees. The $Al_2O_3$ caused more erosion than the road dust. The relative volumes of metal lost due to erosion were 17-4PH and Type 410 stainless steel (about equal) < Ti-6Al-4V < 2024 aluminum. Erosion was about equal on annealed and fully hardened specimens of the same alloy.

The effects of monomethylhydrazine (MMH) on several cryopanel materials has been investigated by ARO.[16] Specimens were exposed 532 hours to MMH at 4 torr at room temperature and at temperatures between 77 and 300 K (-321 and + 81 F). Types of specimens included bare and painted copper, brazed copper, and copper welded to Type 304 stainless steel (nickel welding wire); bare aluminum and Type 304 stainless steel; brazed copper stressed; and copper welded to Type 304 stainless steel stressed. After test, the copper was tarnished and the paint (black epoxy) was blistered and/or separated from the coated panels. Metallographic examination did not reveal any evidence of subsurface attack in any of the materials tested.

The corrosion behavior of metals in Freon-11 at 300 C (572 F) and 60 atmospheres has been studied by Russian scientists.[17] Weight-loss results after 50 hours' exposure are summarized as follows:

| Material | Weight Loss, $mg/cm^2$ |
|---|---|
| Steel | 2.00 to 3.00 |
| 13Cr steel (0.4 C) | 1.40 |
| 17Cr-2Ni steel | 0.33 |
| Titanium | 30.70 |
| Aluminum | 11.70 |
| Copper | 856.0 |
| Brass | 877.0 |

The copper and brass were disintegrating with time, while the rates of attack on the aluminum and titanium were increasing.

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2